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SUMMARY OF RECENT JET PROPULSION LABORATORY RESEARCH ON STORABLE PROPELLANTS

D. R. BARTZ

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PREFACE

This paper was presented to the Working Group on Propellants of the Advisory Panel on Fuels and Lubricants, Department of Defense, on June 19, 1959.

I. INTRODUCTION

Although the Jet Propulsion Laboratory worked on small-scale motors using propellants which now fall into the "storable" category as early as 1947, interest in these propellants was reawakened about three or four years ago. At that time several people at the Laboratory, notably Dr. Homer J. Stewart and Arthur F. Grant, became convinced that much of the development difficulty encountered with the existing ballistic-missile propulsion systems was directly attributable to the cryogenic nature of the oxidizer and the chemically nondescript nature of the fuel. Further, they were concerned with the number of people required for propellant production and handling in the field, and the time required for fueling the missile.

Thus, interest was developed in a group of propellants which contained neither cryogenics nor nondescript hydrocarbons and which, by stretching the imagination and ingenuity only slightly, were storable as liquids over the temperature range required by military applications. This category of propellants became known as "storables" —a term probably only slightly more definitive than the term "high-energy" when related to liquid propellants.

Perhaps the factor that distinguished these propellants from those already long in use on such missiles as the Corporal, the Nike, and others was that the principal interest in storable propellants was as a replacement for LOX-hydrocarbons, which established the initial boundary condition on the propellant selection that there should be no loss of performance. This requirement led to the selection of N₂O₄ as the principal oxidizer candidate over such competitors as hydrogen peroxide and fuming nitric acids. Some interest in ClF₃ was evolved for critically volume-limited systems tempered, however, by the fact that with regard to reactivity ClF₃ is closely

ALL CONTINUES

related to liquid fluorine. Similarly, performance considerations led to the selection of hydrazine as the principal fuel, with some disposition shown toward lower energy fuels such as UDMH, DETA, and hydrazine blends for such advantages as greater thermal stability, lower freezing point, and lower cost. All of these initial considerations have been thoroughly discussed in meetings such as this, and need not be covered in further detail.

Instead, two propellant combinations that were selected by this Laboratory for detailed research study will be discussed, together with the several areas of research directed toward these combinations, such as combustion, heat transfer and cooling, and gas generation. In covering each of these areas, the principal problems, the achievements thus far, and what remains to be accomplished, will be presented in a general way. Further, a bibliography of reports covering recent JPL work or storable propellants is provided.

In the belief that group applied research is best directed when focused on a specific system objective, the development of a small-thrust storable-propellant propulsion system was initiated as a research project of the Power Plant Research Section of the Laboratory in about October 1957. In order to obtain the highest performance from this category of propellants and to face the most difficult problems that might eventually require solution, the propellants selected were N₂O₄ and anhydrous hydrazine. The thrust level selected was the minimum that could be cooled by conventional regenerative techniques and yet be compatible with the Laboratory's facilities; it turned out to be 6000 lb. Design analysis showed that at this thrust level only slight penalty, if any, would be suffered by the use of a gaspressurized feed system instead of a turbopumped system and that the optimum chamber pressure was about 150 psia. A balance of considerations of weight, coolingload addition, and performance gains indicated that an expansion ratio of about 20:1 was the best compromise for this engine.

A few months after the initiation of the project, a decision was made to commit the engine to upper-stage application for the Army *Juno* series, which caused acceleration of the program until about October 1958, when such use was canceled. The program was con-

tinued at a lower level for the next few months as an advance-of-the-art project initially under ARPA and later under NASA.

In about March of this year, the 6K propulsion system, still under development, was again committed to flight application, this time for upper stage of the *Vega*, an early-capability deep-space vehicle of NASA. It has been this propulsion system, now under the project direction of the Propulsion Development Section of the Laboratory, that has motivated much of the research described below.

In addition, however, some injector testing in uncooled thrust chambers at 20,000- and 45,000-lb thrusts was conducted using these propellants during the interval mentioned.

Thus, while the initial interest in storable propellants was as a proposed replacement of LOX-hydrocarbons in ballistic-missile applications, the passage of time and the arrival of the Space Age have shifted the interest toward space applications. Initially, the reasons for selecting storable propellants were centered around a potentially early availability of new systems, but beyond that came considerations of long-term storage of propellants in a space environment, system versatility, system simplicity, and reliability. However, the question of what propellants are actually storable for long periods in space is still open even at this late date.

The other storable-propellant combination that has received attention is that using C1F₃ as the oxidizer and anhydrous hydrazine as the fuel. Work on this combination was initiated because C1F3 was believed to offer a good indictrination into the reactive nature of liquid F2, which was of principal interest but for which facilities were not available. Further, there was some interest in the combination because of its density and impulse, which made it desirable for single-stage ground-based missiles. Because the Laboratory is presently concerned with propulsion for final stages of space vehicles, the interest in the C1F3-hydrazine combination has waned. The intention now is to carry the program only far enough to get the final results of some injector principles developed during the program and to measure heat-flux distribution in a system such as this with the potential for substantial recombination.

II. COMBUSTION

The matters dealt with under this heading include the ignition problem, progress in injector-element design and the effects of injector design on combustion performance and stability, factors affecting monopropellant operation, and studies of C1F₃-hydrazine and aniline combustion.

A. Ignition

One of the problems associated with any propellant combination is that of ignition, especially under vacuum conditions. While it was clear that hydrazine is hypergelic with both N_2O_4 and $C1F_3$ at atmospheric or nearatmospheric pressures, there was a question raised about its behavior in a vacuum. It was found that such a problem did not in fact exist, because in combustion chambers of normal size choked-oxidizer flow was established during the 30-to-60-millisecond oxidizer lead normally provided for these combinations. The choked-oxidizer flow established predictable chamber pressures of a few psia prior to the injection of the fuel in all cases, the ensuing ignition always being smooth and reliable with less than two milliseconds' delay.

B. The Splash-Plate Injector

In initiating the development of the 6K, 20K, and 45K engines, the starting point in each case has been the use of splash-plate injectors. The reasons for this choice revert back to earlier experience with such injectors for use with hydrazine, which was preceded by work in Germany. This earlier work had empirically established the splash-plate injector as being markedly superior to other types of injectors in use at that time for hydrazine. Some physical reasons for its superiority will be discussed below.

The selection of splash-plate injectors for recent engine programs was made in the interest of getting the engines going as soon as possible even though certain reservations were maintained about this type of injector. Specifically, splash-plate injectors have a tendency to be heavy and difficult to construct for large engines, typically give high chamber-heat fluxes because of strong recirculation patterns, and are somewhat prone to com-

bustion instability, although this can be effectively reduced. Splash-plate injectors of the type shown in Fig.1 have given performance results ranging from as low as 90% of equilibrium c^* at best-performance mixture ratio (Fig. 2) to as high as 97%, at L^* values of about 40 in. and contraction ratios from about 1.6 to 2.6 (Fig. 3). With the best injector configurations, a loss of about 4% in performance results from a reduction of L* from 40 in. to 20 in. It was found that the peak-performance mixture ratio could be shifted from approximately 0.7 to 1.1 (compared with the theoretical equilibrium peak at 1.05), by varying design parameters. Changes in such parameters as impingement-point position relative to splash-plate position, number and size of orifices, fluid dynamic characteristics of injected streams as influenced by the injector orifices, splash-plate angle, splash-plate diameter, use of central nonimpinging-fuel jet, and injector pressure drop, were observed to have significant influence on both performance and stability.

Figure 4 gives a typical chamber-pressure record of the 6K engine with 10 psi peak-to-peak acoustic-mode instabilities and 16 psi peak-to-peak random low-frequency chamber-pressure oscillations. Later versions of the injector have succeeded in reducing the magnitude of these oscillations by 50%. In no instance has any particular adverse effect of the oscillations been noted.

C. Combustion Studies

During one phase of the program to investigate the combustion characteristics of the N₂O₄-hydrazine propellant combination, color photographs of combustion at

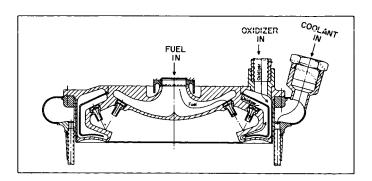


Fig. 1. Splash-Plate Injector

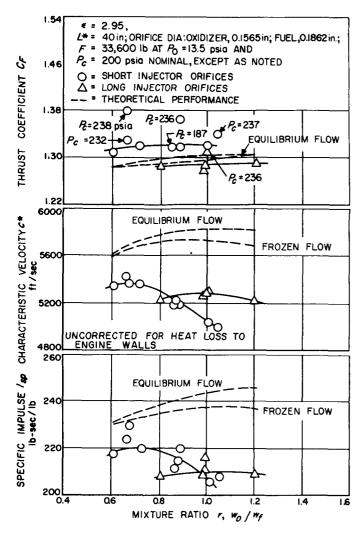


Fig. 2. Performance Data, 45K N₂O₄—N₂H₄ Uncooled Thrust Chamber Tests, Contraction Ratio of 2, Splash-Plate Injector

one atmosphere without a combustion chamber were taken and studied. One such photograph of a single oneon-one impinging-jet element with a 120-deg included angle is reproduced as Fig. 5. The oxidizer jet is on the left and the fuel on the right. Although there is room for some interpretive latitude, those working on the program were convinced that the dark zone on the left (which was dark red) was indicative of heavy oxidizer concentration on the left-hand region of the fan downstream of the impingement point and the lighter region on the right (which was yellow) is indicative of heavy fuel concentration. The white zone in the center is believed to be fully reacted combustion gases. Data from 20K tests with and without splash plates (Fig. 6) show

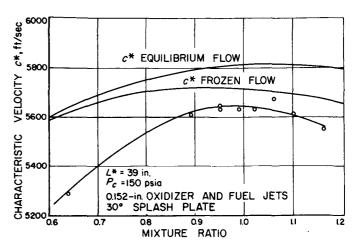


Fig. 3. Performance Data, 6K N₂O₄—N₂H₄ Water-Cooled Thrust Chamber Tests, 30-deg Splash-Plate Injector, with 6% Fuel Through Center Jet

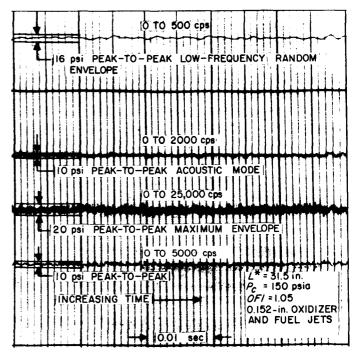


Fig. 4. Chamber-Pressure Stability, Conditions of Fig. 3

the influence of the splash plate on performance. Note the very low performance when the splash plate was omitted.

It has been inferred from such photographs and data that one possible explanation of poor performance with impinging-jet injectors with the N_2O_4 -hydrazine combination is that the initial impact of the propellants evolves gas so rapidly that the gas evolution prevents the bulk

of the propellant masses from ever gaining physical contact with each other in the region of the injector face. Thus the slow diffusion process downstream is required to complete the reaction. This of course leads to large L^* requirements or low performance in ordinary values of L^* .

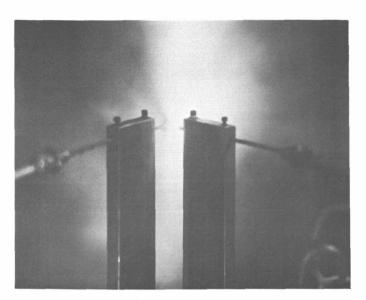


Fig. 5. Combustion, Single Open 120-deg Impinging-Jet Injector Element, Using N₂O₄—N₂H₄

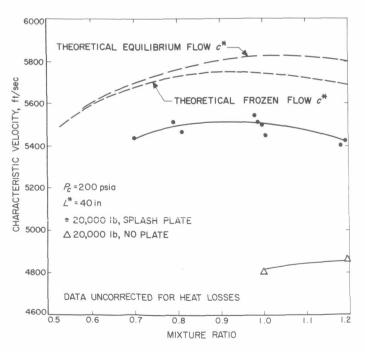


Fig. 6. Effect of Splash Plate on Performance, 20K N₂O₃—N₂H₄ Uncooled Thrust Chamber Tests

A schematic diagram of the deduced combination pattern of an impinging jet-type injector is compared with that of a splash-plate injector in Fig. 7. Note the forced recirculation of the oxidizer and the forced secondary mixing zone near the center of the splash-plate injector. Support for this hypothesis has also been gained from high-speed colored moving pictures of the combustion in transparent combustion chambers at chamber pressures of interest.

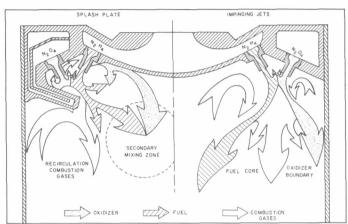


Fig. 7. Deduced Combustion Patterns for Splash-Plate (Left) and Impinging Jet (Right) Injectors, Using N_2O_4 — N_2H_4

D. Concentric-Tube Injectors

Combustion research such as this, as well as studies of liquid-phase reaction rates of numerous propellant combinations, has led to the development of concentrictube or concentric-spray injector elements. Investigations have been carried out with single elements at nominal thrust levels of 40, 80, 200, 300, 500, and 800 lb of thrust per element. A schematic drawing of a 300-lb-thrust element is given in Fig. 8.

Performance levels as high as 97% of equilibrium c^* (i.e., 5650 ft/sec) have been obtained at 40 lb thrust and an L^* of 40 in. (Fig. 9). Similarly, performances of 96% at 300 lb thrust per element at an L^* of 20 in., and 98% at 800 lb thrust per element at an L^* of 30 in., were obtained, with very smooth combustion (Fig. 10).

It is believed that the advantages of this type of injector over the current splash-plate injectors will be greater stability of chamber pressure, lower injection-

pressure drops, possibly reduced heat transfer to the injector face and combustion-chamber walls, and a few percent better performance in somewhat shorter com-

bustion chambers. The benefits derived from this type of injector are believed to be due to finer-scale mixing for a given thrust level per element because of (1) the

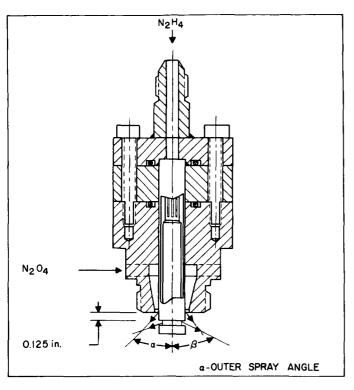


Fig. 8. Concentric-Tube Injector Element

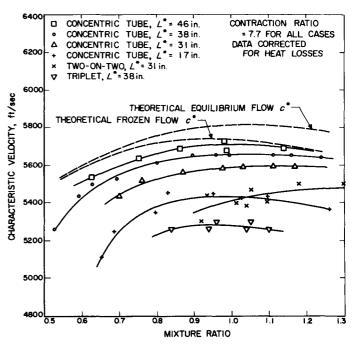


Fig. 9. Performance Data with Concentric-Tube Injector Element of 40 lb Thrust, Contraction Ratio of 7.7, Using N_2O_4 — N_2H_4

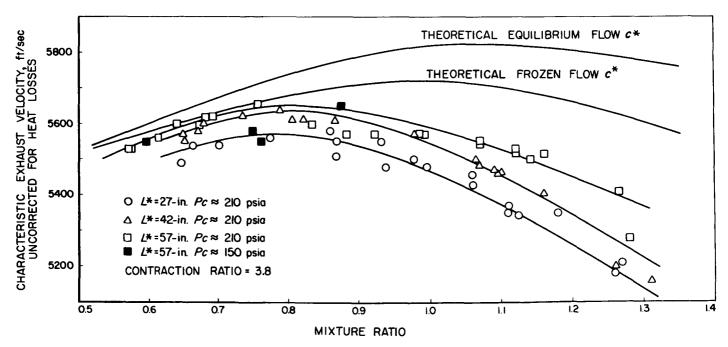


Fig. 10. Performance Data with Concentric-Tube Injector Element of 800 lb Thrust, Contraction Ratio of 3.8, Using N₂O₄—N₂H₄

spreading out of the impingement zone and (2) the tendency for the propellants to be atomized prior to impingement due to hydrodynamic forces. Although injectors consisting of a multiplicity of such elements have not yet been tested, the hope is that the symmetry and the expected self-sufficiency of the combustion-gas cone evolving from each of these elements will allow the stacking of many of them side by side with little or no interaction. If this is demonstrated, it may be possible to achieve large changes in scale by varying the number of such elements.

E. Monopropellant Operation

The consequence of utilizing a fuel which is also a good monopropellant has led to several interesting combustion system concepts.

One concept was to decompose the fuel either thermally or catalytically in an uncooled chamber and then inject the oxidizer into the decomposition-gas flow downstream. The advantage of such a scheme would result from loading the stage oxidizer-lean, so that it would always run out of oxidizer first and continue on to complete fuel exhaustion on monopropellant operation at a respectable performace level. Some preliminary experimental results on such a scheme were encouraging but the work was dropped in favor of more pressing 6K engine problems.

Another possible variation of the scheme, using a topping turbine in the decomposition-gas flow in a similar fashion to the peroxide-JP super-performance engines, was considered but not worked on.

Still another variation would be the use of monopropellant hydrazine decomposition in three auxiliary vernier engines attached to the stage which in principle could provide complete stage-attitude control and terminal-velocity control. In operation, the flow to the vernier-control motors would pass through the main thrust chamber and would be started before the main motor was started to give a stage-separation thrust. By continuing the hydrazine flow after main-engine shutdown, the engine-cooling problem at shutdown would be practically solved. Although this system had many advantages, and a competitive system weight to a gimballed engine system, it was deferred in favor of a gimballed

system in the interest of meeting a tight schedule. It is hoped that work may proceed on this system in the future.

F. C1F₃ Program

The ClF₃ program initiated for the reasons mentioned earlier started out with studies of material compatibility, handling techniques, and small-thrust-injector-element testing with hydrazine as the fuel. The program then proceeded to injector investigations in uncooled thrust chambers at 5000 lb thrust; this is the current phase.

In general, it has been quite easy to get essentially 100% of theoretical equilibrium c^{\bullet} with any one of several types of injectors. It is not clear at this point whether this seeming impossibility is due to uncertainties in the theoretical c^{\bullet} calculations or uncertainties in corrections to the experimental measurements, such as determining the true stagnation pressure or true throat area during hot operation, or assessing the influence of combustion in the nozzle.

The principal difficulty has been in the loss of stainless steel injector parts by local reaction with the ClF₃ on the combustion side. By changing to copper and aluminum injectors this difficulty has been overcome. Except for a persistent low-frequency feed-system instability the combustion has been comparatively smooth in most tests.

The current and anticipated final goals of the program involve the measurement of local heat-flux distributions in a water-cooled sectional thrust chamber. As much as a 35% increase in heat flux due to recombination is theoretically possible for this combustion system.

G. Acid-Aniline Program

One phase of some recent acid-aniline combustion at 20K thrust is also worth mentioning, even through this is of course a low-energy combination. These tests involved the use of new impinging-jet injectors which were designed on the basis of results of an extended program of hydraulic investigations of jets and of the characteristics of the spray fan resulting from the impingement of two jets. From the investigation it was learned how to produce a nearly uniform mixture-ratio distribution throughout the resulting fan using nonreactive liquids,

and what the shape of the iso-mass-flow lines would be. An injector making maximum use of this information in the sizing and placing of the jets was constructed with the same number of pairs of jets as had been used on the standard *Corporal* injector.

Combustion tests showed that the performance was elevated to 98% \pm ½% of equilibrium c^{\bullet} over a mixture ratio range from 2.2 to 3.1, compared with standard Corporal injectors which produce 92% at a mixture ratio of 2.1 and only 88% at 2.8. Furthermore, the level of chamber-pressure fluctuations was reduced to below 1% over the whole range of mixture ratios mentioned whereas the level of instability of the standard Corporal injector

was $\pm 5\%$ at a mixture ratio of 2.1 but a tremendous $\pm 50\%$ at a mixture ratio of 2.8. Finally, the chamber-heat flux measured by short-duration-transient techniques was reduced by about a factor of 2, compared with that of the *Corporal* engine. Again, all that was done to accomplish these startling changes was to make the jet flow more stable, size the jets to give most uniform distribution of mixture ratio in the spray fan, and locate the jets to give the most uniform distribution of mass evolution off of the injector face. It remains to be seen whether or not these principles will be applicable to a highly reactive propellant combination (such as N_2O_4 and hydrazine), which has significantly lower combustion-delay times.

III. HEAT TRANSFER

In the general area of heat-transfer study are discussed considerations of gas-side heat flux, local film cooling, hydrazine as a regenerative coolant, leaks and shutdown problems, and cooling-system tests and designs.

A. Combustion-Side Heat Transfer

An important aspect of the research program has been concerned with the prediction of the distribution of local heat flux throughout thrust chambers. Several years ago a fairly complicated open-form boundary-layer solution for the distribution of convective heat-transfer coefficients was developed and later was closely approximated with a simple closed-form equation.

More recently the program has been devoted to checking the theory with measurements of local heat-flux distribution in motors of 1000- to 2000-lb thrust. Transient and steady-state temperature-gradient techniques as well as steady-state calorimetric techniques have been used successfully—each with a special area of application. Some typical results measured by the calorimetric technique and compared with predictions made with the simple closed-form equation are shown in Fig. 11. The heat-flux distribution in thrust chambers using N_2O_4 —hydrazine is probably one of the most predictable since there is no carbon deposition to cloud the issue, nor is there excessive dissociation with consequent serious recombination effects.

Some film-cooling investigations with both N₂O₄ and hydrazine have revealed that either can be used locally to reduce the heat flux, but that neither is a particularly good film coolant. The program continues in order to establish a better understanding of the factors affecting combustion-side heat transfer and film cooling.

B. Hydrazine Cooling

Although in the early small-thrust investigations hydrazine was employed as a regenerative coolant both with success and with failure, little was known about the cooling limits of hydrazine or the causes of the explosive failures. To accomplish these objectives an investigation of hydrazine heat-transfer characteristics, using electrically heated tubes, was initiated. The program has since been completed and reported.

To summarize, it was found that hydrazine was an unusually good coolant both with and without nucleate boiling. The limiting cooling-rate capability, directly related to the transition from nucleate to film boiling, was vastly superior to any other liquid propellant, and second only to water. It was found that successful cooling with hydrazine could be achieved at these high heat fluxes, so long as the following conditions are carefully avoided:

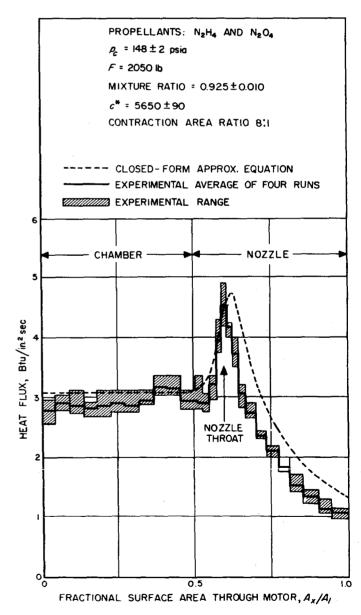


Fig. 11. Comparison of Measurements of Combustion-Side Heat-Flux Distribution with Predictions



(1) local stagnation, which could lead to runaway thermal decomposition, and (2) use of incompatible wall materials or accumulation of contaminants such as rust or finely divided metal particles, which could lead to excessive catalytic decomposition. Electrically-heated-tube tests such as these were discovered to be a fairly sensitive test of material compatibility and came close to modeling conditions to be expected in coolant passages. Thus far all JPL work in this area has been with anhydrous hydrazine, although the effects of additives are currently under study.

C. Special Cooling Tests

Special rocket-motor firing tests have been run to answer questions pertinent to the effect of pinhole leaks, the consequence of a transition to film boiling, and the problem of engine shutdown.

It was found that a clean pinhole leak of about ten thousandths of an inch would cause no particular problem, but would simply establish local film cooling.

The consequence of a burnout or transition to film boiling was found to be the destruction of the particular passage in which it occurs and the probable destruction of downstream manifolds.

The problem of engine shutdown with hydrazine is associated with the quantity of heat transferred to the wall during residual or shutdown combustion and the quantity of heat stored in the hot metal wall. It is believed that as long as the total quantity of heat is insufficient to boost the bulk temperature of the hydrazine above the autoignition temperature, no shutdown failures will occur. Unfortunately, this limiting temperature is a function of the local thermal environment and not strictly a property of the liquid. Values reported lie in the region from 400 to 600°F, with 400°F probably a realistic lower limit for design purposes. The problem of shutting down the 6K engine at the highest bulk temperatures to be expected has not yet been faced. For the present the coolant is being bypassed around the propellant valve after the propellant valve is shut off to provide an extra couple of hundred millisecond of fuel flow after shutoff. Finally, the question of how high an injector-inlet bulk temperature can be safely tolerated with hydrazine has been partially answered with a series of monopropellant-gas-generator tests in which the inlet bulk temperature was increased to the failure limit. It is believed that the limit of safe operation is that which will cause the hydrazine to flash to vapor as it is throttled through the injector.

D. Engine Cooling on the 6K Engine

So far a total of 24 successful water-cooled tests have been made with the 6K engine using two types of thrust chambers. In addition, there have been two short-duration but unsuccessful regenerative tests. The failure is believed due to a structural failure of one of the tubes which is believed to have resulted from local pitting during a pickling operation.

One of the two types of thrust chambers is a tapered-tube tube-wall thrust chamber with the tubes circular in cross-section out to an expansion ratio of about 5. Beyond that the tubes take on a kidney-bean cross-section. Thus, a convoluted inner surface is presented to the combustion-gas flow. The other type of thrust chamber makes use of a smooth-spun inner skin, welded and brazed ribs, and brazed wire-wrapping to form the outer skin. It is interesting to note that about 20% greater total heat transfer has been consistently measured when using the tube-wall thrust chamber under comparable conditions used in tests with the smooth-wall thrust chamber. The difference is believed due to the added surface area presented to the flow.

E. Design Analysis

The results of design analyses of engine cooling show that small low-chamber-pressure engines are cooling-limited by the permissible bulk-temperature rise, whereas local flux rates can be met without too much difficulty. Consequently, fuels that are more volatile than hydrazine, operate at higher mixture ratios, and have poorer specific heats, are less suitable than hydrazine as regenerative coolants under such limiting conditions. At the 6K, 150-psi conditions, even hydrazine is pushed toward its cooling-capacity limit.

Probably up to several times higher thrust and chamber pressures, difficulty could be expected in cooling an engine with other storable fuels such as UDMH unless special innovations are employed such as extensive film cooling, refractory coatings, or uncooled ablating materials over a major part of the expansion cone. All of these are possible but tend to penalize the system. At the thrust levels and chamber pressures of current ballistic missile engines UDMH would probably serve ade-

quately as the fuel coolant with the help of some film cooling in the high-flux regions, and would probably be preferred from the standpoint of fuel stability, ease of injector development and propellant cost. The only negative aspect would probably be the small performance penalty compared with hydrazine.

IV. MISCELLANEOUS

In addition to the areas covered, the Laboratory's work has encompassed other problems that can only be listed by subject, but which are documented to some extent in the Bibliography. These additional areas are:

- 1. The use of hydrazine monopropellant decomposition products for the pressurization of propellants. Systems considered include combinations with (a) helium pressurizing the oxidizer, hydrazine-decomposition gases pressurizing the fuel, (b) oxidizer-rich bipropellant combustion gases pressurizing the oxidizer, hydrazine-decomposition gases pressurizing the fuel, (c) hydrazine-decomposition gases pressurizing both fuel and oxidizer using bladders, and (d) hydrazine-decomposition gases pressurizing both fuel and oxidizer directly.
- 2. The use of small hydrazine monopropellant motors to provide either vernier corrections of axial velocity

or lateral velocity for corrective maneuvers of payloads.

- 3. Corrosion and materials compatibility with storable propellants, including decomposition-rate measurements in bombs, with investigation of the influence of additives.
 - 4. Decomposition of hydrazine by radiation.
- 5. Effect of impact of incendiary bullets and high velocity projectiles on storable propellants in storage vessels.
- 6. Research on diffusers for sea-level testing of low-chamber-pressure—high-expansion-ratio thrust chambers. In this area the application of diffusers is being extended to more severe conditions than can be satisfied with the straight-tube diffusers through the use of a second throat and secondary mass flow.

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